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| <b>14. ABSTRACT</b><br>This grant has as its overall objective to understand and manipulate the chemistry at intermetallic particles (IP's) at Al alloy surfaces. The purpose is to control corrosion of alloys that contain such particles. This long range goal is being addressed through four major tasks. These are: 1) use scanning electrochemical microscopy and other imaging techniques to investigate the local cathodic and anodic reactivity of intermetallic inclusions at the alloy surface, 2) investigate dioxygen reduction at the intermetallic inclusions and how to control it, 3) study the use of strongly adsorbing species to poison the reduction of dioxygen at the surfaces of intermetallic particles, and 4) examine the mechanism by which conducting polymers influence the open circuit behavior of these alloys, also with a mind to decreasing the tendency for dioxygen reduction at the intermetallic particles. |                                    |   |   |   |  |
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## "Nanoscale Surface Chemistry of Intermetallic Inclusions at Aluminum Alloy Surfaces"

October 29, 2004

submitted by: Prof. Daniel A. Buttry, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838; voice: (307) 766-6677; fax: (307) 766-2807; email: Buttry@uwyo.edu

## 1. Brief Summary of Research Activities

We have made progress in several areas during the past grant period. First, both SECM and fluorescence microscopy have been successfully used to image cathodic activity at intermetallic particles at the AA2024 surface. Second, we have very recently succeeded in using real-time fluorescence microscopy to indirectly image  $O_2$  reduction at the AA2024 surface. In this experiment, the  $OH^-$  generated by  $O_2$  reduction is used to produce the emissive form of a fluorophore. Through a variety of processes, the fluorophore production is limited to the region near the IP, allowing us to indirectly image  $O_2$  reduction at the IP's in real-time with sub-micron resolution. Third, a wall-jet flow cell experiment has been used to study dioxygen reduction at IP's. During these experiments we discovered significant damage (trenching) around IP's due to hydroxide production during  $O_2$  reduction. This damage is substantially suppressed by buffers that act against local pH increases, suggesting some new strategies for protective coatings. Fourth, we have just completed a study of the protective action of a conductive polymer coating comprised of a poly(aniline) blend with poly(methylmethacrylate). We find that the coating protects the Al alloy by poisoning its potential in a region where  $O_2$  reduction is kinetically inhibited.

## 2. Major Accomplishments

The use of both scanning electrochemical microscopy (SECM) and real-time fluorescence microscopy to study local redox reactivity at the alloy surface has progressed significantly during the past year. In the SECM method, we use a micron-sized Pt microelectrode probe tip that senses the products of local redox reactions at the IP's that are exposed at the alloy surface. This experiment can be done in several different modes of operation. So far, we have focused on imaging reductive (cathodic) activity at the IP's. SECM images are correlated with scanning electron micrographs and energy dispersive spectroscopic (EDS) mapping of the surface, which reveals elemental distributions and allows identification of the various IP's. In this way, we can understand the cathodic reactivity of the individual types of IP's. Figure 1 above shows an example of an SECM image of cathodic activity toward a solution phase redox couple serving as a surrogate for  $O_2$ .

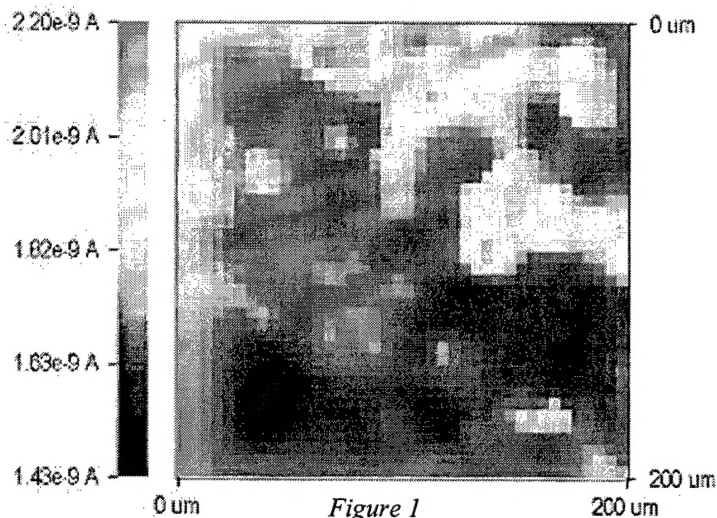


Figure 1

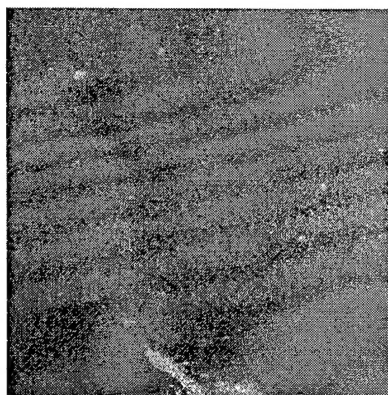
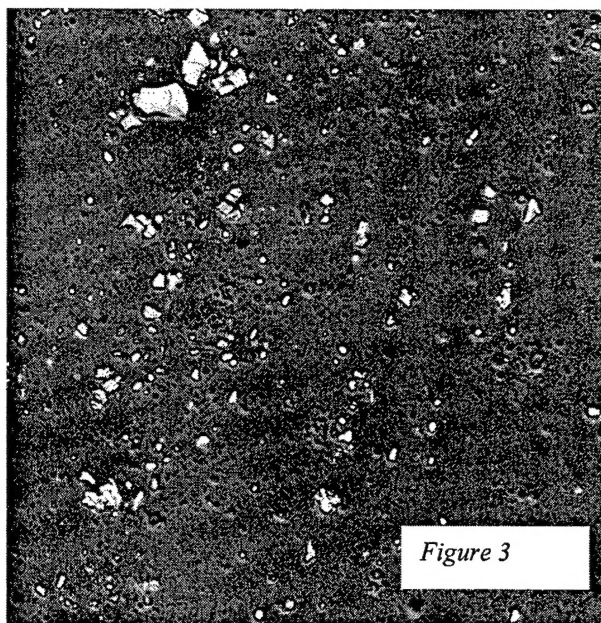


Figure 2

We have very recently succeeded in using fluorescence microscopy to indirectly image  $O_2$  reduction at individual IP's in real-time. In this experiment, the  $OH^-$  generated by  $O_2$  reduction is used to produce the emissive form of fluorescein. Through a variety of processes (including use of buffers and photobleaching), the fluorophore production is limited to the region near the IP. This experiment gives a real-time fluorescence intensity signal that is directly proportional to the current for  $O_2$  reduction at individual IP's. We have observed several very interesting features in these images. First, we see some large, very bright IP's that seem to be continuously generating  $OH^-$ . Second, we see some medium sized IP's whose fluorescence intensity is highly variable on a timescale of a few seconds. Third, we see some very small objects (we are

not certain if these are IP's or defects in the oxide layer) that literally flash on and off. This is the first real-time information of this type ever available, and we expect it to be critical in understanding how individual IP's of differing composition (such as  $\text{Al}_6(\text{Fe}, \text{Cu}, \text{Mn})$  and  $\text{Al}_2\text{Cu}$ ) respond to treatments designed to inhibit  $\text{O}_2$  reduction. It may also be useful in providing the basic science for new approaches to monitoring for corrosion failure. We will soon have a link from our web page (<http://www.uwyo.edu/chemistry/faculty/buttry.htm>) that will give access to a video of fluorescence intensity versus time for dioxygen reduction experiments of this type that were done on a confocal laser scanning microscope in the UW Microscopy facility. The image in Figure 2 shows a single frame of that movie, in which the bright green objects correspond to IP's that are actively producing  $\text{OH}^-$  from  $\text{O}_2$  reduction. Because of the frame rates available from a variety of fluorescence microscopy techniques, it is possible to either watch this process in real-time (using a conventional fluorescence microscope) or to employ slower methods capable of sectioning the fluorescence intensity in the direction normal to the surface (using a confocal laser scanning microscope). Both approaches are being actively pursued.



Various studies of dioxygen reduction are being done using both a wall-jet electrode flow cell and rotating disk electrodes (RDE). The wall-jet experiments allow us to easily switch between flow streams that are purged with either dinitrogen or dioxygen, while the RDE experiments give a simple way to quantitatively the  $\text{O}_2$  reactivity under different conditions. Both provide a fast and relatively straightforward assay of the total reactivity of the surface toward dioxygen reduction. A significant finding in the past year is that  $\text{O}_2$  reduction at IP's and the consequent production of  $\text{OH}^-$  causes trenching around the IP's, as well as activating the surface toward the  $\text{O}_2$  reduction reaction. Figure 3 shows an example of this damage at its initial stages. We also find that buffers substantially inhibit this damage. These findings are significant because they show that AA2024 and related alloys may be susceptible to damage under conditions (aerated, neutral, chloride-free solutions) that were previously viewed as benign. Work in this area is continuing with further studies of buffer protection. This work may point the way toward new protective coating formulations.

Finally, we have explored the protective mechanisms for conducting polymer blends of poly(aniline) and poly(methylmethacrylate). In these experiments, we have used open circuit measurements and SECM to monitor the behavior of an AA2024 sample coated with a thin film of the blend and then intentionally damaged it by scratching. We have found that the blend poises the open circuit potential at a value sufficiently positive so that  $\text{O}_2$  reduction cannot occur at significant rates. In contrast, during the PMMA control experiment, the OCP drifts rapidly negative after the scratch, producing conditions where both  $\text{O}_2$  and solvent (water) can be reduced. This produces  $\text{OH}^-$  and ultimately leads to the type of damage shown above in Figure 3. We are proceeding with additional experiments in this area.

### 3. Technology Transitions

I have initiated a consulting relationship with Luna Innovations in Blacksburg, VA which is attempting to develop new chemical pretreatments for Al alloys that can be used prior to application of various corrosion protection coatings. They are seeking SBIR support for development of their ideas.

### 4. Personnel supported on the grant

Undergraduate student associated with the project: Alyssa Pollock (support from NSF-REU)

Daniel A. Buttry, PI, 1/2 to 1 month summer

Jesse Seegmiller, Ph. D. graduate student (100%)

Reinaldo Bazito, postdoctoral fellow (50-100%, depending on month)

## 5. List of Publications

1. "A SECM Study of Heterogeneous Redox Activity at AA2024 Surfaces." Seegmiller, J. C.; Buttry, D. A.. *J. Electrochem. Soc.* **2003**, *150*(9), B413-B418.
2. "Visualization of Cathode Activity for Fe-Rich and Cu-Rich Intermetallic Particles via Cathodic Corrosion from Dioxygen Reduction at Aluminum Alloy 2024-T3", Seegmiller, J. C.; Bazito, R. C.; Buttry, D. A., *Electrochem. Solid-State Lett.* **2004**, *7*(1), B1-B4.
3. "Mechanism of Action of a Corrosion Protection Coating for AA2024-T3 Based on a Poly(aniline)-Poly(methylmethacrylate) Blend", Jesse C. Seegmiller, José E. Pereira da Silva, Daniel A. Buttry, Susana I. Córdoba de Torresi, and Roberto M. Torresi, *J. Electrochem. Soc.*, **in press**.
4. Chemical heterogeneities in AA2024: dioxygen reduction as a probe of removal of Cu-rich inclusions via chemical etching, J. Seegmiller; Y. Kondratenko; G. Chen; D. A. Buttry, *Proc. - Electrochem. Soc.*, 2001-22, 1124 (**2001**).
5. Adsorption of polyphosphonates on native aluminum oxide, R. C. Bazito; D. A. Buttry, *Proc. - Electrochem. Soc.*, 2003-25, 241 (**2004**).
6. Influence of local redox activity at Al alloys on corrosion, J. C. Seegmiller; R. C. Bazito; D. A. Buttry, *Proc. - Electrochem. Soc.*, 2003-23, 29 (**2004**).

## 6. List of Presentations

1. "Selective Etching of Intermetallic Inclusions from the Surface of Aluminum AA2024 Alloys", G. Chen, M. Williams, J. Malmberg, J.-S. Kim and D. A. Buttry, invited presentation at the Spring Meeting of the Electrochemical Society, Toronto, 1999.
2. "A Mild Chemical Etching Bath for Selective Removal of Intermetallic Inclusions from the Surface of Aluminum AA 2024-T3 Alloys", G. Chen, M. Williams, J. Malmberg, J.-S. Kim and D. A. Buttry, presentation at the 2000 Meeting of the Electrochemical Society, Phoenix.
3. "Chemical Heterogeneities in AA2024: Dioxygen Reduction as a Probe of Removal of Cu-Rich Inclusions via Chemical Etching", Guoying Chen, Jesse Seegmiller and Daniel A. Buttry, presentation at the 2001 Meeting of the Electrochemical Society, San Francisco.
4. "Electrochemical Reactivity at Heterogeneous Alloy Surfaces: Wall-Jet Flow Cell and SECM Studies", Jesse Seegmiller and Daniel A. Buttry, presentation at the 2002 Spring Meeting of the Electrochemical Society, Philadelphia.
5. "SECM Studies of Heterogeneous Redox Reactivity at an Al Alloy Containing Fe- and Cu-Rich Intermetallic Particles", Jesse Seegmiller and Daniel A. Buttry, presentation at the 2002 Fall Meeting of the Electrochemical Society, Salt Lake City.
6. "SECM Studies of Heterogeneous Redox Reactivity at an Al Alloy Containing Fe- and Cu-Rich Intermetallic Particles", J. Seegmiller and D. Buttry (invited paper in Symposium on Electrochemistry at Nanoscale Dimensions), presentation at the 2002 Fall Meeting of the Electrochemical Society, Salt Lake City, UT.
7. "Dioxygen Reduction at AA2024 Causes Base-Induced Loss of Passivation" J. Seegmiller, R. Bazito, and D. Buttry, Abstract #302, presentation at the 2003 Spring meeting of the Electrochemical Society, Paris, France.
8. "Corrosion Inhibition on an Aluminum Alloy by an Acrylic Conducting Blend" J. Seegmiller, D. Buttry, J.E. Pereira da Silva, S.I. Córdoba de Torresi, and R.M. Torresi, Abstract #323, presentation at the 2003 Spring meeting of the Electrochemical Society, Paris, France.
9. "Influence of Local Redox Reactivity at Al Alloys on Corrosion" J. Seegmiller, R. Bazito, and D. Buttry, Abstract #489, presentation at the 2003 Fall meeting of the Electrochemical Society, Orlando, FL.
10. "Adsorption of polyphosphonates on native aluminum oxide" Bazito, Reinaldo C.; Buttry, Daniel A., presentation at the 2003 Fall meeting of the Electrochemical Society, Orlando, FL.
11. "SECM Studies of Corrosion Protection Coatings on Al Alloys" J. Seegmiller, J. Pereira da Silva, D. Buttry, S. Cordoba de Torresi, and R. Torresi, Abstract #843, presentation at the 2003 Fall meeting of the Electrochemical Society, San Antonio, TX.